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H. Bernas, A. Traverse, F.C. Zawislak[+], J. Chaumont[*] and L. Dumoulin[**]

Institut de Physique Nucléaire, B.P. N°1, 91400 Orsay, France.
[*] *Laboratoire René Bernas, 91400 Orsay, France,*
[**] *Laboratoire de Physique des Solides, 91400 Orsay, France.*

Abstract. - Ion implantation simultaneously produces compositional changes and radiation damage in the target. If the latter is not annealed, amorphization should ultimately result. Can implantation of a covalent solute into a transition metal host stabilize the damage and hence produce an amorphous alloy at lower concentrations than other techniques ? We have studied the composition-dependence of the resistivity and TCR of thin (600-800 Å) Pd films implanted at 6 K with Si ions. The results are compared to those obtained on the corresponding well-documented quench-condensed alloys, which are amorphous at Si concentrations ∿.18.
The resistivity of the implanted films saturates at about 90 μΩ·cm for Si concentrations above ∿.18. Thus, the critical concentration for amorphization is presumably the same for the low-temperature implanted or quench-condensed Pd-Si alloy, confirming that local structure effects dominate amorphous alloy formation criteria.
In a further experiment, hydrogen was implanted into the amorphous Pd-Si films (again at 6K). The resistivity increased sharply, doubling at H concentrations around 100 %. The resulting systems were superconducting; their maximum critical temperature was 2.6 K.

Introduction :

We have investigated the production of amorphous alloys by low-temperature ion implantation. When keV -ions penetrate into a solid, collisions between the incoming ion and target atoms result in large displacement rates and, for doses high enough to produce significant concentration changes, a high disorder level. If the implantation temperature is sufficiently low, damage annealing should be considerably impeaded and production of an amorphous system may result. The possibility of such an amorphization process was demonstrated some time ago [1,2].

In the present work, we have studied the resistivity and the temperature-coefficient of the resistivity (TCR) of silicon-implanted palladium thin films (implantation temperature 6K). The quench-condensed Pd-Si alloy has been extensively investigated [3,4] and the structural, thermodynamic and electrical properties are well-known. A comparison of the latter systems with the corresponding ion-implanted alloys of the same nominal composition was thought to be of interest. Specifically, we set out to determine whether the critical composition for amorphous alloy formation depends on the preparation technique. The final position of the implanted atom is strongly correlated with the target atom displacement cascade, so that the following question arose : can the implantation of a covalent impurity into a transition metal host stabilize the implantation -induced damage and hence produce and amorphous alloy at lower concentrations than otherwise obtainable ?

Experiment and results:

Palladium films (thickness ≃800 Å) were prepared by evaporation of high-purity Pd on quartz substrates in ultra-high vacuum [5]. The residual resistivity of the films was typically about 5.5 μΩ.cm, and the resistivity ratio for an 800 Å film was typically 2.9. Silicon was implanted at temperatures below 6K at two energies and increasing doses in order to obtain a homogeneous distribution of the solute atoms in the Pd films. The homogeneity of the implanted Si profile and the changes in film thickness due to sputtering [6] were monitored by in situ Rutherford backscattering (RBS) experiments [7] using the alpha-particle beam of the ion-implanter itself with the sample kept at 6 K.

Homogeneous films were obtained by Si ion implantation at mean energies of 80 and 20 keV.

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The dose-dependence of the film resistivity was measured up to doses of about 1.10^{17} Si/cm^2. The results are displayed in Figure 1. As determined by RBS measurements, the maximum Si concentration in these experiments was approximately 22 at %. The saturation value of the film resistivity (90 μΩ.cm) is reached at a Si concentration of 18 at %; these are practically the values obtained for samples prepared by quench-condensation, whose amorphous nature was determined by their radial distribution function [2]. No superconductivity was found in these films down to 1.7 K.

Low-energy (4 keV) hydrogen ions were implanted into these films (with Si concentrations of about 20 at %) without warming up (i.e., at 6K). The resistivity of the $Pd_{.8}Si_{.2}H_y$ films increased sharply in the range $0<y<1.$; a saturation value of about 170 μΩ.cm is reached when $y > 1.$ at % (figure 1). The hydrides were found to be superconducting at least above $y=.75$ (they are in fact probably superconducting at somewhat lower hydrogen concentrations). The maximum superconducting critical temperature was 2.6 K; the transition widths were quite narrow (typically 0.1 K).

Isochronal annealing measurements performed up to 300 K on the $Pd_{.8}Si_{.2}H_2$ film revealed that desorption starts at about 80 K and takes place gradually. At 300 K, all the hydrogen has desorbed. Subsequent cooling to 80 K allowed us to measure the temperature coefficient of the resistivity of $Pd_{.8}Si_{.2}$. This provided a value of $(4\pm1)\times10^{-4}$ K^{-1}; the resistivity temperature-dependence was found to be linear.

Discussion and conclusion :

At present, we have no way of checking directly the amorphous (or crystalline) nature of our low temperature-implanted samples <u>in situ</u>. Such a check would require, e.g., an on-line electron microscope to obtain diffraction patterns. In the absence of such direct evidence, we rely on the conduction data obtained in the present experiments. Table I presents the resistivity and TCR values for ion-implanted and quench-condensed "amorphous" alloys as well as for the corresponding system in the crystalline state. Our ion-implantation data are in very good agreement with results on quench-condensed systems whose amorphous nature was confirmed by X-ray diffraction experiments.

This leads us to conclude that the critical Si concentration for amorphous Pd-Si alloy formation is the same for low-temperature ion implanted alloys and for quench-condensed alloys. Amorphous alloy formation criteria are thus probably determined by the necessity of producing a well-defined local structure even under the extreme conditions prevailing in the present experiments.

Our measurement of the superconducting critical temperature T_c in the Pd-Si hydride warrants comparison with the result obtained by Stritzker and Luo [8] on quench- condensed Pd-Si into which hydrogen had been implanted. At implanted hydrogen concentrations of 100 %, the quench- condensed $Pd_{.8}Si_{.2}$ hydride and the ion-implanted $Pd_{.8}Si_{.2}$ hydride both display the same value of T_c. This is of course further support for the conclusion that quench-condensation and ion implantation lead to very similar structures, at least in this particular case.

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	Crystalline	Amorphous (quench condensed)	Implanted
ρ(μΩcm)	$9^{(4)}$	$80^{(2)}$ $86 \pm 15^{(4)}$ $86^{(3)}$	89
TCR (K^{-1})	9×10^{-3} (4)	$\geq 7.10^{-5}$ and $\leq 2.6 10^{-4}$ (4) $7.5\ 10^{-3}$ (3)	$(4\pm1)\times10^{-4}$

Table I : Resistivities and TCR in crystalline and amorphous state of quench-condensed $Pd_{.8}$ $Si_{.2}$ and implanted $Pd_{.78}$ $Si_{.22}$

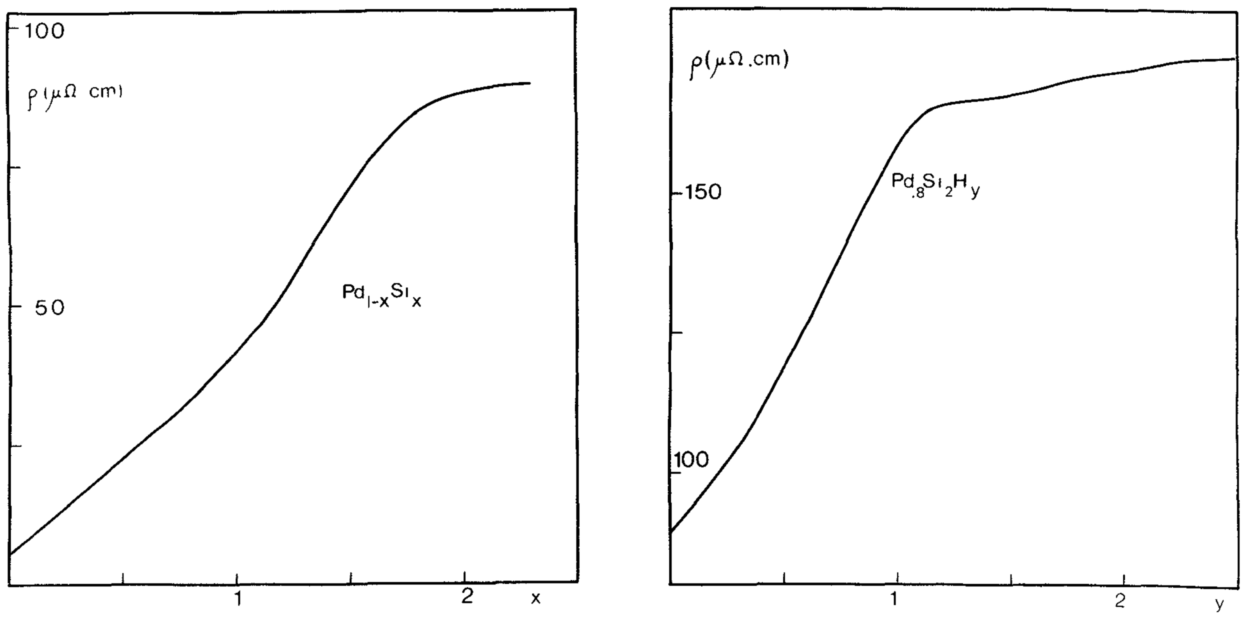

Fig. 1 : Resistivity dose dependence of $Pd_{1-x}\,Si_x$ and $Pd_{.8}\,Si_{.2}\,H_y$

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+ visitor from Instituto de Fisica, UFRGS, Brazil.